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(54) **BLOWN POLYPROPYLENE RESIN CONTAINER**

GEBLASENER BEHÄLTER AUS POLYPROPYLENHARZ

RECIPIENT EN RESINE POLYPROPYLENIQUE SOUFFLEE

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D scriptionTECHNICAL FIELD

5 The present invention concerns an injection stretch blow molded container made of a polypropylene resin having excellent transparency and strength and with less odors.

BACKGROUND ART

10 Since polypropylene series resins are excellent, for example, in heat resistance, chemical resistance and steam barrier property, as well as blow molded products (hollow molded containers) thereof are also excellent in the rigidity and impact shock resistance, they are generally used for tableware containers, detergent containers, medical contain-
 15 ers for fluid supplementation. However, the blow molded containers made of polypropylene having such excellent properties have a problem in that the transparency is insufficient. In particular, high transparency is required in the medical containers for fluid supplementation so that obstacles in the liquid contents can be observed.

Heretofore, as a method of improving the transparency of polypropylene molded products, there has been pro-
 posed, for example, to apply heat molding with addition of a nucleating agent such as dibenzilidene sorbitol or di
 (alkylbenzilidene)sorbitol (refer to Japanese Unexamined Patent Publication Nos. 22740/1976, 117044/1978,
 30449/1981 and 225143/1983).

20 However, when the polypropylene resin is molded under heating being blended with dibenzilidene sorbitol or di
 (alkylbenzilidene)sorbitol, odors are caused during heat molding and the resultant molding products have odors. In a
 case of using them as containers for fluid supplementation, there is also a safety and sanitary problem such as leaching
 of the nucleating agent to the fluid supplementation.

For overcoming such a problem, there has been proposed a method of adding a high molecular compound such
 25 as 3-methylbutene-1 polymer or vinyl cycloalkane polymer as a nucleating agent (refer to Japanese Examined Patent
 Publication No. 32430/1970 and Japanese Unexamined Patent Publication No.139731/1985) but higher transparency
 has been demanded.

FR-A-1 434 150 discloses a polymer composition having a moldability better than that of propylene homopolymer
 containing an isotactic propylene and a second α -olefine. 3-Methyl-butene-1 may be used as the second α -olefine.
 30 There is no indication in the reference that an injection stretch-blow molding may be used as a molding method of the
 polymer composition. Further, the reference teaches that the transparency tends to lower at the molding temperature
 of from 200° to 300°C and that the transparency lowers when cooled at a low speed.

EP-A-0 251 340 relates to an injection stretch-blow molding and provides a molded product having a high trans-
 parency. The reference teaches that the high transparency is achieved by selecting the specific molding conditions
 35 and that the injection molding temperature is from 200° to 260°C.

DISCLOSURE OF THE INVENTION

40 The present invention concerns a blow molded container made of polypropylene resin obtained by injection stretch
 blow molding of a polypropylene resin stretching, in which the polypropylene resin comprises a polypropylene polymer
 composition containing from 0.0001 to 10% by weight of a 3-methylbutene-1 polymer, as well as medical instruments
 comprising such a blow molding container.

As the degree of crystallinity of the 3-methylbutene-1 polymer used in the present invention is higher, it can provide
 greater effect for improving optical properties. As one of the measures for indicating the degree of the crystallinity,
 45 melting point or heat of fusion measured by a differential scanning calorimeter is used.

The 3-methylbutene-1 polymer used in the present invention has a melting point preferably higher than 300°C and
 a heat of fusion preferably at least 37.674 J/g (9 cal/g). Those with the melting point lower then 300°C or with a heat
 of fusion of less than 9 cal/g are not preferred since the effect for improving the optical property is insufficient. The
 3-methylbutene-1 polymer has, more preferably, a melting point of higher than 303°C and a heat of fusion of at least
 50 62.79 J/g (15 cal/g) and, most preferably, a melting point of at least 305°C and a heat of fusion of at least 66.976 J/g
 (16 cal/g).

Within the range for satisfying the above-mentioned conditions, the 3-methylbutene-1 polymer used in the present
 invention may be a copolymer with other α -olefin having 2 to 18 carbon atoms, but it is, preferably, a homopolymer.

As a catalyst system used for obtaining the 3-methylbutene-1 polymer described above, a Ziegler-Natta catalyst
 55 capable of providing a polymer, particularly having a high stereo regularity, is used.

Such a catalyst is described in, for example, Japanese Examined Patent Publication Nos. 27871/1979, 8451/1980,
 8452/1980, 8003/1980, 39165/1980 and 14054/1980.

For instance, there has been used suitably a catalyst system with an aluminum content of not more than 0.15 as

expressed by the ratio of atoms of aluminum to titanium and comprising a solid titanium trichloride catalyst complex containing a complexing agent, an organic aluminum compound or, further, an electron donating compound as the third ingredient such as ether, ester, amine or amide.

As an example for the solid titanium trichloride catalyst complex, there can be mentioned a solid titanium trichloride compound obtained by reducing TiCl_4 with an organic aluminum compound represented by the general formula $\text{AlR}_n\text{X}_{3-n}$ (where R represents a hydrocarbon group of 1 to 20 carbon atoms, preferably, an alkyl group with 1 to 20 carbon atoms and, more preferably, an alkyl group with 2 to 6 carbon atoms, X is a halogen atom and n is 1 to 3), then applying a treatment with a complexing agent having an electron donating atom or group such as ether, thioether, amine, amide, ketone, ester or phosphine and, depending on the case, further with CCl_4 or TiCl_4 ; or a solid titanium trichloride compound deposited from a homogeneous liquid hydrocarbon solution comprising TiCl_3 and a complexing agent having an electron donating atom or group such as ether and, optionally TiCl_4 , by means of heating or by treatment with TiCl_4 ; or a solid titanium trichloride compound deposited by reducing TiCl_4 with an organic aluminum compound represented by the general formula $\text{AlR}_n\text{X}_{3-n}$ (where R, X and n are the same as described above) under the presence of a complexing agent having an electron donating atom or group such as ether. The complexing agent described above is selected from the group consisting of ethers, thioethers, amines, amides, ketones, esters and phosphines. There are used, preferably, ethers and, more preferably, dialkyl ethers with 3 to 10 carbon atoms.

As an example for the dialkyl ether, there can be mentioned, for example, di-n-butyl ether, di-n-amyl ether, dioctyl ether, didecyl ether, amyl butyl ether, ethyl hexyl ether or hexyl octyl ether.

In addition for increasing the degree of crystallinity higher for the 3-methylbutene-1 polymer used in the present invention, it is preferred to polymerize 3-methylbutene-1 by an amount greater than 10 g per one gram of a solid titanium trichloride catalyst complex under the presence of a catalyst in which an aluminum content to titanium is not greater than 0.15 as expressed by the ratio of atoms of aluminum to titanium and comprising a solid titanium trichloride catalyst complex containing a complexing agent, an organic aluminum compound and, further, an electron donating compound.

The amount of the 3-methylbutene-1 polymer in the propylene polymer is from 0.0001 to 10% by weight, preferably, from 0.0003 to 3% by weight. If the content of the 3-methylbutene-1 polymer is too low, the effect for improving the transparency is insufficient. On the other hand, if the content of the 3-methylbutene-1 polymer is too high, it is not so preferred since there are such problems as occurrence of fish eyes, reduction of the transparency due to the 3-methylbutene-1 polymer per se and increase of the cost.

As the process for producing a propylene polymer composition containing a 3-methylbutene-1 polymer used in the present invention, there can be mentioned a process for polymerizing 3-methylbutene-1 by using a Ziegler-Natta catalyst and then conducting homopolymerization of propylene or copolymerization of propylene with other α -olefin of 2 to 18 carbon atoms under the presence of the resultant 3-methylbutene-1 polymer or a process of preparing a polymer as a master batch in the above-mentioned process and then mixing it with a homopolymer of propylene or a copolymer of propylene and other α -olefin.

For the polymerization of propylene or propylene and other α -olefin with 2 to 18 carbon atoms in the succeeding step of the former process, polymerization is attained for at least 500 g, preferably, at least 1,000 g and, more preferably, at least 2,000 g based on one gram of the solid catalyst ingredient, although being related with the amount of polymerization for 3-methylbutene-1.

If the polymerization amount of propylene based on the solid catalyst ingredient is lower than the above-specified range, the nuclei-forming ability per 3-methylbutene-1 polymer is reduced.

In the latter process, there is no particular limit for the content of the 3-methylbutene-1 polymer in the propylene polymer composition containing the 3-methylbutene-1 polymer prepared by the former process, but it is less than 10% by weight and, preferably, less than 5% by weight. The mixing method may be a usual method, for example, by an extruder, a Brabender kneader or a roll.

Upon mixing, it is desirable to conduct kneading within such a temperature range as not melting the 3-methylbutene-1 polymer. As the starting propylene polymer used in admixture with the 3-methylbutene-1 polymer, there can be mentioned a propylene homopolymer or a random or block copolymer of propylene and other α -olefin (ethylene or other α -olefin with upto 12 carbon atoms) (the copolymerizing ratio of ethylene or other α -olefin is upto 15% by weight and, preferably, from 0.1 to 5.0% by weight).

There is no particular limit for the melt flow rate (hereinafter simply referred to as MFR) of the polypropylene resin, those within a range usually from 0.2 to 50 g/10 minutes, desirably, 0.4 to 30 g/10 minutes as expressed by a value measured in accordance with the method of JIS K-7210, at 230°C and under a load of 2.16 kg are preferably used.

Further, it is also possible to properly blend and use various kinds of additives generally blended with polypropylene resins, for example, anti-oxidant, lubricant, antistatic agent, anti-blocking agent, and known polymers, fillers, such as rubber, silica, or the like.

In the present invention, an injection blow molded container (hollow molded container) is manufactured by using the propylene polymer containing the 3-methylbutene-1 polymer and subjecting the same to the injection stretch blow molding (stretch blow molding).

That is, a hollow container is manufactured by molding a bottomed parison by injecting a molten resin of the propylene polymer into a die at a temperature of 190 to 290°C, applying preliminary blowing if desired, and then applying stretch blow molding under the conditions of a resin temperature at 90 to 150°C, and at a stretching ratio of 1.2 to 3.5 times (preferably, 1.2 to 2.2 times) in the longitudinal direction and 1.2 to 6.0 times (preferably, 1.5 to 5.0 times) in the lateral direction. The wall thickness of the bottomed parison ranges from 1.5 to 6 mm. The bottomed parison may be cooled to solidify (cold parison) and then applied with stretch blow molding by reheating to the resin temperature as described above or the shape of the parison can be retained without cooling to solidify the bottomed parison. Further, it may be taken out of a die while at least a portion of the parison is still in a molten state (hot parison) and then applied with stretch blow molding at the resin temperature described above. The stretch blowing process is conducted by a method of combining mechanical longitudinal stretching by a stretching rod and a blow stretching by air blowing (lateral stretching).

BEST MODE FOR CARRYING OUT THE INVENTION

Examples will be shown below but the present invention is not restricted to the following Examples. Values for the physical property in the subsequent examples were measured in accordance with the following methods.

(1) Melt Flow Rate (MFR)

Measured in accordance with JIS K-7210 (230°C, under a load of 2.16 kg)

(2) Crystallizing Temperature (T_c)

Measured at a temperature elevating and falling rate at 10°C/min using a DSC2C type differential scanning calorimeter manufactured by Perkin-Elmer Co.

(3) Parallel Light Transmittance

Parallel light transmittance (%) was determined by using Clarity Meter TM-ID Model manufactured by Murakami Shikisai Institute, setting the total light transmittance as 100, projecting a spot at the center for each of the portions of a bottle container, rotating the bottle container by one turn, taking out only the direct light (parallel light) and reading the maximum amount of light thereof.

(4) Heat Resistance

The container body was punched into a rectangular piece (15 mm × 50 mm) and annealed in air at 120°C-1 hr. Subsequently, after leaving it in a thermostat chamber at 23°C and 65% for 24 hrs, shrinkage along the direction of height *1 and along the circumferential direction *2 were measured.

*1) Shrinkage in the longitudinal direction of a rectangular piece 50 mm in height × 15 mm in circumferential direction.

*2) Shrinkage in the longitudinal direction of a rectangular piece 15 mm in height × 50 mm in circumferential direction.

(5) Strength

Tensile impact strength along the direction of the height of the container was measured by punching the container body in accordance with ASTM D 1822-63.

(6) Odor Evaluation Method

① Evaluation Method

Specimens each cut into about 5 mm square were charged by 10 g in a 250 cc Erlenmeyer flask and tightly capped. Evaluation for odors was conducted by leaving them under the condition at a temperature of 40°C for 48 hours.

② Judging Method for Odor

Evaluation was made for 1-5 five steps. 1: scarcely smelling, 2: slightly smelling, 3: smelling, 4: strongly smelling, 5: very strongly smelling.

Evaluation was made by five persons and the average value was calculated by counting fractions of 0.3 and over and cutting away the rest.

(7) Leaching Test

Leaching test was conducted according to a test method for plastic container for use in fluid supplementation as specified in the general test method of Japanese Pharmacopoeia, and it was judged as satisfactory or failure.

EXAMPLE 1

(a) Catalyst Preparation Example

At room temperature, 515 ml of purified toluene was charged into a one liter volume autoclave sufficiently substituted with nitrogen and 65.1 g (0.5 mol) of n-butyl ether, 94.9 g (0.5 mol) of titanium tetrachloride and 28.6 g (0.24 mol) diethyl aluminum chloride were added, under stirring, to obtain a homogenous brown solution. Then, the temperature was elevated to 30°C. After elapse of 30 min, the temperature was elevated to 40°C and kept at 40°C as it was for 2 hours. Subsequently, 32 g (0.17 mol) of titanium tetrachloride and 15.5 g (0.058 mol) of tridecylmethacrylate were added and the temperature was elevated to 98°C. After maintaining at 98°C for 2 hours, granular purple solids were separated and washed with toluene to obtain solid titanium trichloride.

(b) Resin Production Example-1

(Production of propylene polymer master batch containing 3-methylbutene-1 polymer)

At room temperature, 1.2 mmol of diethyl aluminum chloride was added under argon sealing into a 2 liter magnetic induction stirring type autoclave sufficiently substituted with purified argon and, further, 700 cc of liquid 3-methylbutene-1 was charged.

Then, the temperature was elevated to 70°C and 3-methylbutene-1 was polymerized for one hour with addition of 91 mg of the solid catalyst ingredient obtained in the catalyst preparation example. Subsequently, after purging all of the amount of 3-methylbutene-1, 3 mmol of diethyl aluminum chloride and 0.12 mmol of methylmethacrylate were supplemented additionally. An H₂ pressure was set to 0.5 kg/cm² and 700 g of propylene was further added to conduct homopolymerization of propylene. After 30 minutes, propylene was purged and the catalyst was removed with a mixed solvent of isobutanol-n-hexane to obtain 271 g of a propylene polymer composition including the 3-methylbutene-1 polymer.

The amount of a 3-methylbutene-1 polymer obtained in an experiment conducted under identical polymerization conditions but with no propylene polymerization was 10.8 g.

The 3-methylbutene-1 polymer had a melting point of 311°C and a heat of fusion of 20 cal/g.

The content of the 3-methylbutene-1 polymer in the propylene polymer composition calculated based on the yield of the 3-methylbutene-1 polymer was 4.0% by weight.

This propylene polymer composition had MFR of 0.27 g/10 minutes, a melting point of 163.4°C and a crystallizing temperature of 126.6°C.

(c) Resin Production Example-2

1.27 parts by weight of the propylene polymer composition obtained in Resin Production Example-1, 0.1 part by weight of calcium stearate as a stabilizer, 0.2 part by weight of BHT (2,6-di-t-butylhydroxy toluene) and 0.08 part by weight of Illuganox 1010 {tetrakis[methylene-3-(3',5'-di-t-butyl-4-hydroxyphenyl)propionate]methane, antioxidant manufactured by Ciba Geigy Co} were added to 100 parts by weight of a propylene-ethylene random copolymer (trade name: Mitsubishi Polypro 6200EI, manufactured by Mitsubishi Kasei Co., melt flow rate: 3.2 g/10 min, density: 0.894 g/cm³, melting point: 135°C, crystallizing temperature: 95°C) and, after mixing in a Henschel mixer, they were pelletized by a 50 mmφ extruder into pellets. The content of the 3-methylbutene-1 polymer in the resin composition was 0.05% by weight.

(b) Production of Injection Stretch Blow Molding (biaxial stretch blow molding) Container

Pellets obtained in Resin Production Example-2 were injected by using a biaxial stretch blow molding machine (Model SB-150 III, manufactured by Aoki Institute) into a die at a surface temperature of 20°C under the conditions of a resin temperature of 240°C and an injection pressure of 60 kg/cm² and then taken out from the die. The bottomed parison had a stretched diameter portion of 24.0 mm ϕ , a stretched body length of 50 mm and a body wall thickness of 4.0 mm. The molded conditions were 7.0 sec of injection time and 2.5 sec of cooling time and the product was taken out from the die. The temperature of the body portion of the bottomed parison was 111°C.

For the temperature of the body portion of the bottomed parison, the temperature at the surface of the parison body was measured by using a digital radiation thermometer (Model IR-AH, manufactured by Chino Co.).

The resultant bottomed parison at a high temperature was put into a blow mold and it was stretched in the longitudinal direction by introducing a stretching rod to the inside of the bottomed parison and pressing the bottom of the bottomed parison and a pressurized air of 10 kg/cm² was blown for five seconds around the end of the longitudinal stretching to obtain a blown biaxially stretched bottle. The temperature of the blow mold in this case was 15°C and the bottle was cooled after the completion of the blowing and taken out from the blow mold. The resultant bottle had about 80 mm height and about 60 mm ϕ diameter at the stretched body portion. The thickness was about 0.3 mm also as the thickness for the body portion.

For the resultant bottle, transparency (parallel light transmittance), heat resistance, leaching test and odor were evaluated. The results are shown in Table 1.

EXAMPLES 2-6

The procedures were the same as in Example 1 except for changing the blending amount of the 3-methylbutene-1 polymer and the conditions for injection stretch blow molding into those conditions shown in Table 1. The results are shown in Table 1.

EXAMPLES 7-8

At room temperature, 800 ml of purified n-hexane and then 13.0 mmol of diethyl aluminum chloride and 4,000 mg of the solid catalyst ingredient obtained in Catalyst Preparation Example 1 were added under argon sealing to a 2 liter magnetic induction stirring type autoclave sufficiently substituted with purified argon and the temperature was elevated to 70°C. Then, 206 ml of 3-methylbutene-1 was charged to conduct polymerization of 3-methylbutene-1 at 70°C for 30 minutes.

Subsequently, unreacted 3-methylbutene-1 was purged and washing was conducted with purified n-hexane.

The amount of 3-methylbutene-1 formed was 11.0 g based on one gram of the solid catalyst ingredient.

The 3-methylbutene-1 polymer had a melting point of 308°C and a heat of fusion of 16 cal/g.

Then, at room temperature 52 mmols of diethyl aluminum chloride, 1.7 mmols of methylmethacrylate and 9 liters of purified n-hexane were added, under argon sealing, to a 24 liter magnetic induction stirring type autoclave sufficiently substituted with purified argon and an H₂ pressure was set to 0.3 kg/cm². Then the temperature was elevated to 70°C and 1,330 mg of the catalyst ingredient obtained as described above was introduced as a Ti catalyst ingredient, and propylene was added in such an amount as to control the propylene pressure at 6 kg/cm³ and homopolymerization of propylene was conducted. After 4.5 hours, propylene was purged and the catalyst was removed by a mixed catalyst of isobutanol-n-hexane to obtain 4,890 g of a propylene polymer composition including the 3-methylbutene-1 polymer.

The content of the 3-methylbutene-1 polymer in the propylene polymer composition was 0.299% by weight.

Subsequently, a resin composition of propyleneethylene random copolymer was obtained in the same procedures as those in Resin Production Example-2 except for using one part by weight of the polymer (Example 7) or 0.16 part by weight of the polymer (Example 8) in Resin Production Example-2 instead of 1.27 parts by weight of the polymer obtained in the Resin Production Example-1.

Injection stretch blow molding was conducted by using the resin thus obtained and molding was conducted in the same molding conditions as those in Example 2.

The results are shown in Table 1.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Kind of nucleating agent	3-methyl-butene-1 polymer	3-methyl-butene-1 polymer	3-methyl-butene-1 polymer	3-methyl-butene-1 polymer	3-methyl-butene-1 polymer	3-methyl-butene-1 polymer	3-methyl-butene-1 polymer	3-methyl-butene-1 polymer
Content of nucleating agent (wt%)	0.05	0.05	0.05	0.10	0.10	0.10	0.003	0.0005
Molding condition	Injection molding temperature (°C)	240	240	240	240	240	240	240
	Parison temperature (°C)	111	109	103	111	109	109	109
	Longitudinal stretching ratio (times)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Lateral stretching ratio (times)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	Wall thickness of bottle (μm)	300	300	300	300	300	300	300
Transparency (parallel light transmittance) (%)	26	19	16	26	22	16	21	18
Odor (score)	2	1	1	2	1	1	1	1
Heat resistance (shrinkage in the direction of height/circumference(%))	2.5/2.6	3.0/2.6	6.8/4.4	2.8/2.5	2.8/2.5	5.2/4.0	3.1/2.7	3.3/3.0
Leaching test	pass	pass	pass	pass	pass	pass	pass	pass
Strength [Tensile impact strength (kg·cm/cm ²)]	400	450	600	420	520	630	450	450

COMPARATIVE EXAMPLES 1-3

The procedures were the same as those in EXAMPLE 1 except for carrying out them under the injection stretch blow molding conditions shown in Table 2 without blending the 3-methylbutene-1 polymer at all.

The results are shown in Table 2.

COMPARATIVE EXAMPLES 4-6

The procedures were the same as those in EXAMPLE 1 except carrying out them while replacing the 3-methylbutene-1 polymer with a commercially available nucleating agent: dibenzilidene sorbitol (Denon YK-1, trade name of product manufactured by Marubishi Yuka Co.) and under injection stretch blow molding conditions as shown in Table 2. The results are shown in Table 2.

5

0

5

0

15

10

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50

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Table 2

	Compara- tive Example 1	Compara- tive Example 2	Compara- tive Example 3	Compara- tive Example 4	Compara- tive Example 5	Compara- tive Example 6
Kind of nucleating agent	-	-	-	Dibenzili- dene sorbitol	Dibenzili- dene sorbitol	Dibenzili- dene sorbitol
Content of nucleating agent (wt%)	-	-	-	0.3	0.3	0.3
Molding condi- tion	240	240	240	240	240	240
	111	109	103	111	109	103
	1.5	1.5	1.5	1.5	1.5	1.5
	2.5	2.5	2.5	2.5	2.5	2.5
Longitudinal stretching ratio (times)						
Lateral stretching ratio (times)						
Wall thickness of bottle (μm)	300	300	300	300	300	300
Transparency (parallel light transmittance) (%)	18	16	12	26	19	16
Odor (score)	1	1	1	5	5	4
Heat resistance (shrinkage in the direction of height/circumference(%))	6.3/4.4	7.0/5.0	10.5/10.5	2.8/2.2	2.8/2.2	4.8/3.8
Leaching test	pass	pass	pass	failed	failed	failed
Strength (Tensile impact strength ($\text{kg}\cdot\text{cm}/\text{cm}^2$))	300	380	560	520	530	640

COMPARATIVE EXAMPLES 7-9

(a) Production of Resin Composition

A polypropylene resin composition containing a 3-methylbutene-1 polymer was obtained in the same manner as in example 7 except for changing the blending amount of the 3-methylbutene-1 polymer to the conditions in Table 3.

(b) Production of Extrusion Blow Molded (direct blow molded) Container

The pellets obtained by the above-mentioned method were formed into a parison by using a blow molding machine (Model BA-2, manufactured by Sumitomo Juki) in an extruding amount of 8 kg/H and a resin temperature of 220°C. Then, after the parison was clamped in a die at 25°C, air was blown and then the product was taken out from the die. The parison had an inner diameter of 36 mmφ, an outer diameter of 40 mmφ and a wall thickness at the body portion of about 2 mm.

The parison obtained was charged into a blow mold and then stretched laterally by blowing a pressurized air at 6 kg/cm² for 20 seconds as molding conditions to obtain a bottle.

The resultant bottle had an inner height of 140 mm, a diameter of 80 mmφ and the wall thickness at the body portion of about 0.6 mm.

For the resultant bottle, transparency (parallel light transmittance), odor and strength were evaluated. The results are shown in Table 3.

COMPARATIVE EXAMPLES 10-13

An extrusion blow molding container was obtained in the same procedures as those in Comparative Example 7 except for replacing the nucleating agent with those shown in Table 3. The results are shown in Table 3.

Table 3

	Comp.-Ex. 7	Comp.-Ex. 8	Comp.-Ex. 9	Comp.-Ex. 10	Comp.-Ex. 11	Comp.-Ex. 12	Comp.-Ex. 13
Kind of nucleating agent	3-methyl-butene-1 polymer	3-methyl-butene-1 polymer	3-methyl-butene-1 polymer	not added	Dibenzilidene sorbitol	Dibenzilidene sorbitol	Dibenzilidene sorbitol
Content of nucleating agent (wt%)	0.05	0.1	0.3	0	0.1	0.2	0.3
Molding condition	Injection molding temperature (°C)	220	220	220	220	220	220
	Parison temperature (°C)	220	220	220	220	220	220
	Lateral stretching ratio (times)	2	2	2	2	2	2
	Wall thickness of bottle (μm)	600	600	600	600	600	600
Transparency (parallel light transmittance) (%)	8	9	8	6	10	16	20
Odor (score)	2	2	2	2	5	5	5
Strength (Tensile impact strength (kg-cm/cm ²))	300	300	300	300	300	320	330

Industrial Applicability

The blow molded container made of a polypropylene resin according to the present invention is improved with the transparency, mechanical strength, odor and safe and sanitary property, and it can be used suitably, for example, to medical containers for fluid supplementation or tableware containers.

Claims

1. A blow molded container made of a polypropylene resin obtained by injection stretch blow molding of a polypropylene resin, characterized in that the polypropylene resin contains from 0.0001 to 10 % by weight of a 3-methylbutene-1 polymer.
2. The blow molded container made of a polypropylene resin according to Claim 1, wherein the 3-methylbutene-1 polymer has a melting point of at least 300°C and a heat of fusion of at least 37.674 J/g (9 cal/g).
3. The blow molded container made of a polypropylene resin according to Claim 1, wherein the 3-methylbutene-1 polymer has a melting point of at least 303°C and a heat of fusion of at least 62.79 J/g (15 cal/g).
4. The blow molded container made of a polypropylene resin according to Claim 1, wherein the 3-methylbutene-1 polymer has a melting point of at least 305°C and a heat of fusion of at least 66.976 J/g (16 cal/g).
5. The blow molded container made of a polypropylene resin according to Claim 1, wherein the polypropylene resin is a propylene polymer composition obtained by:

preliminarily polymerizing 3-methylbutene-1, under the presence of a catalyst with an aluminum content of not more than 0.15 as expressed by the ratio of atoms of aluminum to titanium and comprising a solid titanium trichloride catalyst complex containing a complexing agent and an organic aluminum compound, and occasionally, an electron donating compound, in an amount of greater than 10 g based on 1 g of said solid titanium trichloride catalyst complex, and then

polymerizing propylene or propylene and other α -olefin of 2 to 18 carbon atoms by at least 500 g based on 1 g of said solid titanium trichloride catalyst complex.
6. The blow molded container made of a polypropylene resin according to Claim 1, wherein the polypropylene resin is a mixture of (i) a propylene polymer composition and (ii) a propylene homopolymer or a copolymer of propylene with α -olefin of 2 to 18 carbon atoms,

said propylene polymer composition (i) being obtained by:

preliminarily polymerizing 3-methylbutene-1, under the presence of a catalyst with an aluminum content of not more than 0.15 as expressed as by the ratio of atoms of aluminum to titanium and comprising a solid titanium trichloride catalyst complex containing a complexing agent and an organic aluminum compound, and occasionally, an electron donating compound, in an amount of greater than 10 g based on 1 g of said solid titanium trichloride catalyst complex, and then

polymerizing propylene or propylene and other α -olefin of 2 to 18 carbon atoms in an amount by at least 500 g based on 1 g of said solid titanium trichloride catalyst complex.
7. The blow molded container made of a polypropylene resin according to Claim 1, wherein the injection stretch blow molding is a molding method, which comprises injecting a molten resin of a propylene polymer composition containing from 0.0001 to 10% by weight of a 3-methylbutene-1 polymer at a temperature of 190 to 290°C into a mold thereby forming a bottomed parison, and then applying, with or without preliminary blowing, stretch blow molding under the conditions at a resin temperature of 90 to 150°C and a stretching ratio of 1.2 to 3.5 times in the longitudinal direction and 1.2 to 6.0 times in the lateral direction.
8. Medical instruments comprising a blow molded container made of a polypropylene resin according to Claim 1.

Patentansprüche

1. Blasgeformter Behälter aus einem Polypropylenharz, erhalten durch Spritz-Streckblasen eines Polypropylenharzes, dadurch gekennzeichnet, daß das Polypropylenharz von 0,0001 bis 10 Gew.-% eines 3-Methylbuten-1-Polymers enthält.
2. Blasgeformter Behälter aus einem Polypropylenharz nach Anspruch 1, worin das 3-Methylbuten-1-Polymer einen Schmelzpunkt von mindestens 300°C und eine Schmelzwärme von mindestens 37,674 J/g (9 cal/g) hat.
3. Blasgeformter Behälter aus einem Polypropylenharz nach Anspruch 1, worin das 3-Methylbuten-1-Polymer einen Schmelzpunkt von mindestens 303°C und eine Schmelzwärme von mindestens 62,79 J/g (15 cal/g) hat.
4. Blasgeformter Behälter aus einem Polypropylenharz nach Anspruch 1, worin das 3-Methylbuten-1-Polymer einen Schmelzpunkt von mindestens 305°C und eine Schmelzwärme von mindestens 66,976 J/g (16 cal/g) hat.
5. Blasgeformter Behälter aus einem Polypropylenharz nach Anspruch 1, worin das Polypropylenharz eine Propylenpolymer-Zusammensetzung ist, die erhalten ist durch:

vorheriges Polymerisieren von 3-Methylbuten-1 in Gegenwart eines Katalysators mit einem Aluminiumgehalt von nicht mehr als 0,15, ausgedrückt durch das Atomverhältnis von Aluminium zu Titan, der einen festen Titantrichlorid-Katalysatorkomplex umfaßt, der ein Komplexbildungsmittel und eine organische Aluminiumverbindung und, gelegentlich, eine Elektronen abgebende Verbindung, in einer Menge von mehr als 10 g, bezogen auf 1 g des festen Titantrichlorid-Katalysatorkomplexes, enthält und dann Polymerisieren von Propylen oder Propylen und anderem α -Olefin mit 2 bis 18 Kohlenstoffatomen in einer Menge von mindestens 500 g, bezogen auf 1 g des festen Titantrichlorid-Katalysatorkomplexes.
6. Blasgeformter Behälter aus einem Polypropylenharz nach Anspruch 1, worin das Polypropylenharz eine Mischung von (i) einer Propylenpolymer-Zusammensetzung und (ii) einem Propylenhomopolymer oder einem Copolymer von Propylen mit α -Olefin mit 2 bis 18 Kohlenstoffatomen ist,

wobei die Propylenpolymer-Zusammensetzung (i) erhalten ist durch: vorheriges Polymerisieren von 3-Methylbuten-1 in Gegenwart eines Katalysators mit einem Aluminiumgehalt von nicht mehr als 0,15, ausgedrückt durch das Atomverhältnis von Aluminium zu Titan, der einen festen Titantrichlorid-Katalysatorkomplex umfaßt, der ein Komplexbildungsmittel und eine organische Aluminiumverbindung und, gelegentlich, eine Elektronen abgebende Verbindung, in einer Menge von mehr als 10 g, bezogen auf 1 g des festen Titantrichlorid-Katalysatorkomplexes, enthält und dann Polymerisieren von Propylen oder Propylen und anderem α -Olefin mit 2 bis 18 Kohlenstoffatomen in einer Menge von mindestens 500 g, bezogen auf 1 g des festen Titantrichlorid-Katalysatorkomplexes.
7. Blasgeformter Behälter aus einem Polypropylenharz nach Anspruch 1, worin das Spritz-Streckblasen ein Formverfahren ist, das das Spritzen eines geschmolzenen Harzes aus einer Propylenpolymer-Zusammensetzung, enthaltend von 0,0001 bis 10 Gew.-% eines 3-Methylbuten-1-Polymers, bei einer Temperatur von 190 bis 290°C in eine Form, wodurch ein mit Boden versehener Vorformling gebildet wird, und dann Anwenden, mit oder ohne vorheriges Blasen, eines Streckblasformens unter den Bedingungen einer Harztemperatur von 90 bis 150°C und eines Streckverhältnisses vom 1,2- bis 3,5-fachen in der Längsrichtung und vom 1,2- bis 6,0-fachen in der seitlichen Richtung, umfaßt.
8. Medizinische Instrumente, umfassend einen blasgeformten Behälter aus einem Polypropylenharz gemäß Anspruch 1.

Revendications

1. Récipient moulé par soufflage constitué d'une résine de polypropylène obtenue par moulage par injection-soufflage avec étirage d'une résine de polypropylène, caractérisé en ce que la résine de polypropylène contient de 0,0001 à 10 % en poids d'un polymère du 3-méthylbutène-1.
2. Récipient moulé par soufflage constitué d'une résine de polypropylène selon la revendication 1, dans lequel le

polymère du 3-méthylbutène-1 a un point de fusion d'au moins 300°C et une chaleur de fusion d'au moins 37,674 J/g (9 cal/g).

3. Récipient moulé par soufflage constitué d'une résine de polypropylène selon la revendication 1, dans lequel le polymère du 3-méthylbutène-1 a un point de fusion d'au moins 303°C et une chaleur de fusion d'au moins 62,79 J/g (15 cal/g).

4. Récipient moulé par soufflage constitué d'une résine de polypropylène selon la revendication 1, dans lequel le polymère du 3-méthylbutène-1 a un point de fusion d'au moins 305°C et une chaleur de fusion d'au moins 66,976 J/g (16 cal/g).

5. Récipient moulé par soufflage constitué d'une résine de polypropylène selon la revendication 1, dans lequel la résine de polypropylène est une composition de polymère du propylène obtenue :

en soumettant à une polymérisation préliminaire du 3-méthylbutène-1, en présence d'un catalyseur ayant une teneur en aluminium non supérieure à 0,15, exprimée par le rapport des atomes d'aluminium aux atomes de titane et comprenant un complexe de catalyseur de trichlorure de titane solide contenant un agent complexant et un composé organique de l'aluminium, et, éventuellement, un composé donneur d'électrons, dans une quantité supérieure à 10 g pour 1 g de ce complexe de catalyseur de trichlorure de titane solide, puis en polymérisant du propylène ou du propylène et une autre α -oléfine ayant de 2 à 18 atomes carbone, à raison d'au moins 500 g pour 1 g dudit complexe de catalyseur de trichlorure de titane solide.

6. Récipient moulé par soufflage constitué d'une résine de polypropylène selon la revendication 1, dans lequel la résine de polypropylène est un mélange (i) d'une composition de polymère du propylène, et (ii) d'un homopolymère du propylène ou d'un copolymère du propylène avec α -oléfine ayant de 2 à 18 atomes carbone,

cette composition de polymère du propylène (i) étant obtenue :

en soumettant à une polymérisation préliminaire du 3-méthylbutène-1, en présence d'un catalyseur ayant une teneur en aluminium non supérieure à 0,15, exprimée par le rapport des atomes d'aluminium aux atomes de titane et comprenant un complexe de catalyseur de trichlorure de titane solide contenant un agent complexant et un composé organique de l'aluminium, et, éventuellement, un composé donneur d'électrons, dans une quantité supérieure à 10 g pour 1 g dudit complexe de catalyseur de trichlorure de titane solide, puis en polymérisant du propylène et du propylène et une autre α -oléfine ayant de 2 à 18 atomes carbone dans une quantité d'au moins 500 g pour 1 g dudit complexe de catalyseur de trichlorure de titane solide.

7. Récipient moulé par soufflage constitué d'une résine de polypropylène selon la revendication 1, dans lequel le moulage par injection-soufflage avec étirage est un procédé de moulage qui comprend l'injection d'une résine fondue d'une composition de polymère du propylène contenant de 0,0001 à 10 % en poids d'un polymère du 3-méthylbutène-1 à une température de 190 à 290°C dans un moule, en formant ainsi une paraison munie d'un fond, puis la mise en oeuvre, avec ou sans soufflage préliminaire, d'un moulage par soufflage avec étirage dans les conditions d'une température de résine de 90 à 150°C et d'un rapport d'étirage de 1,2 à 3,5 fois dans la direction longitudinale et de 1,2 à 6,0 fois dans la direction latérale.

8. Instruments médicaux comprenant un récipient moulé par soufflage constitué d'une résine de polypropylène selon la revendication 1.